



**IN THE
UNITED STATES
PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Gordon et al.

CASE: CER-041004

SER. NO.: 10/708,565

FILING DATE: March 11, 2004

FOR: GAS DIFFUSION ELECTRODE
AND CATALYST FOR
ELECTROCHEMICAL
OXYGEN REDUCTION

STATEMENT OF BASIS
FOR RELEVANCE OF
FOREIGN LANGUAGE
DOCUMENTS
IDENTIFIED IN
SUBMITTED PTO-1449

COMMISSIONER FOR PATENTS
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ATTENTION OF:

EXAMINER:

Dear Sir:

If any charges or fees must be paid in connection with the following communication, they may be paid out of our Deposit Account No. 50-0545.

TITLE OF ARTICLE

Kinetics of Cathodic Oxygen Reduction on
Lanthanum-based Perovskite-type Oxides

BASIS FOR RELEVANCE

The kinetics of the electrochemical O₂ reduction on fifteen lanthanum-based Perovskite-type oxides in alkaline solution were examined systematically by use of a rotating ring-disk electrode (RRDE, Fig. 1). The electrode activities of the majority of Oxides (the disk currents) increased with an increase in mixing ratio of respective oxides to carbon (Fig. 2). The number of electrons (n) associated with O₂ reduction was 2.3 ~ 4.0 on oxide (80 wt%)-carbon (20 wt%) electrodes, in contrast to 2.0 on the pure carbon electrode (Fig. 3).

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Oxygen Reduction Activities of Praseodymium Manganites in Alkaline Solution

A series of praseodymium manganites, $\text{Pr}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$ $0 \leq x \leq 1.0$), were examined for their electrode-catalytic activities as incorporated into a gas diffusion-type oxygen reduction electrode working in an alkaline solution. Among the oxides tested, $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ gave the highest electrode performance ($320 \text{ mA} \cdot \text{cm}^{-2}$ at -150 mV vs. Hg/HgO) in $8 \text{ mol} \cdot \text{dm}^{-3}$ KOH aqueous solution at 60°C under air flow. The electrode performances were found to be well correlated with the activities of the oxides for the 4-electron reduction of oxygen ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$) evaluated from a rotating ring-disk electrode analysis. The oxidation state of Mn ions of the oxides was investigated by means of iodometry, X-ray photoelectron spectroscopy, temperature-programmed oxygen desorption and electron spin resonance. The results obtained suggest that the active sites for the 4-electron reduction of oxygen involve Mn^{3+} ions and that their activities increase profoundly as the Mn^{3+} ions neighbor Mn^{4+} to form $\text{Mn}^{3+}\text{-Mn}^{4+}$ pairs. The electrode loaded with $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{Mn}_3$ was confirmed to continue to work rather stably for a test period of 200h under the galvanostatic condition of $300 \text{ mA} \cdot \text{cm}^{-2}$, the oxide being kept intact as revealed by X-ray diffraction analysis after the test. The same electrode was shown to exhibit a promising performance when incorporated into a zinc-air cell.

Electrochemical Oxygen Reduction Properties of Perovskite-type Oxides $\text{La}_{1-x}\text{AzMnO}_3$ ($\text{A}=\text{Na}, \text{K}, \text{Rb}$) in Concentrated Alkaline Solution

Oxygen reduction properties of gas diffusion-type electrodes loaded by 50 wt% with perovskite-type oxides, $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A}=\text{Na}, \text{K}, \text{Rb}$, $0.0 \leq x \leq 0.2$), were investigated in $8 \text{ mol} \cdot \text{dm}^{-3}$ KOH aqueous solution at 60°C under air flow. Among these oxides, $\text{La}_{0.8}\text{Rb}_{0.2}\text{MnO}_3$ gave the highest electrode performance, *i.e.*, current density of $341 \text{ mA} \cdot \text{cm}^{-2}$ at -150 mV vs. Hg/HgO . This oxide was found to be highly active for the direct 4-electron reduction of oxygen as revealed

Mn-Based Perovskite-Type Oxides as Oxygen Reduction Electrode Catalysts for Meta-Air Batteries

by a rotating ring-disk electrode (RRDE) analysis. Electrode performances changed with a change in A or x over the oxides, and tended to be higher with the oxide which exhibited a smaller amount of oxygen desorption in temperature-programmed desorption (TPD) experiments.

On the basis of the iodometry and electron spin resonance (ESR) analysis, the 4-electron reduction was suggested to take place most favorably at the sites composed of a pair of Mn^{3+} and Mn^{4+} on the oxide surface. The electrode loaded with $\text{La}_{0.8}\text{Rb}_{0.2}\text{MnO}_3$ was confirmed to be fairly stable over a continuous operation for 100 h under a galvanostatic condition of 300 mA cm^{-2} . The same electrode allowed to construct a zinc-air battery with a maximum power density as large as 293 mW cm^{-2} at a cell voltage of 0.7 V.

Development of high performance oxygen reduction electrodes (gas diffusion type) is highly desired for realizing metal air batteries with large power. The development should be explored from two standpoints, i.e., establishment of the electrode catalysts which are active, stable from degradation during use and low cost, and establishment of the preparation methods which allows high dispersion of the electrode catalysts on the carbon substrate. These two approaches are demonstrated in this article by taking Mn-based perovskite-type oxides as oxygen reduction electrode catalysts. Among the rare earth metal (Ln)-containing manganites (LnMnO_3), the electrocatalytic activity tended to increase with increasing the ionic radius of Ln^{3+} , becoming the largest with La followed narrowly by Pr. It was shown that, like the case of LaMnO_3 , the partial substitution of Pr in PrMnO_3 for Ca promoted the catalytic activity remarkably, so that the electrode using the oxide of an optimized composition ($\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$) exerted oxygen reduction


performances even better than a Pt-based carbon electrode of commercial origin. In order to demonstrate the importance the high dispersion of oxide catalysts over the carbon substrate, a new preparation method using reverse micelles was investigated by taking LaMnO₃ as an example. Despite the relatively low specific activity of the oxide used, the electrode prepared by the reverse micelle method exhibited performances far better than any of the conventional electrodes so far fabricated. The excellent performances could be ascribed to the high dispersion of LaMnO₃ particles as observed with TEM.

Should anything further be required, a telephone call to the undersigned at (312) 226-1818 is respectfully invited.

Respectfully submitted,

FACTOR & LAKE, LTD.

Dated: January 21, 2005

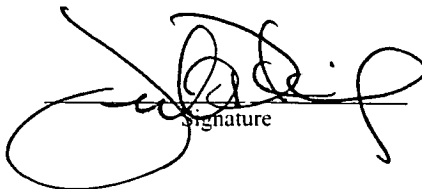

Jacob D. Koering
One of Attorneys for Applicant

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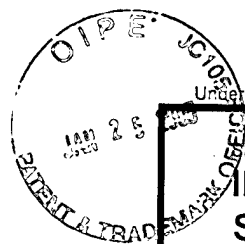

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (use as many sheets as necessary)				Application Number	10/708,565
				Filing Date	March 11, 2004
				First Named Inventor	Gordon et al.
				Art Unit	
				Examiner Name	
Sheet	1	of	2	Attorney Docket Number	CER 041004

U.S. PATENT DOCUMENTS					
Examiner Initials*	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number - Kind Code ² (if known)			
		US-6,060,420	05-09-2000	Munakata et al.	
		US-6,129,862	10-10-2000	Munakata et al.	
		US-6,428,722	08-06-2002	Furuya	
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